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6. AUTHORS
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14. ABSTRACT
This project has been focused on understanding and controlling the electronic properties of graphene using scanning tunneling spectroscopy and optical spectroscopy. By using boron nitride as a substrate underneath graphene we have significantly improved the device quality. We have found that the periodic potential from the boron nitride can modify the band structure of the graphene. The boron nitride also changes the Raman spectrum of the graphene. We have also explored the role of adding additional layers to graphene and different stacking configurations. A third aspect of the project has studied modification

15. SUBJECT TERMS
Graphene, Scanning Probe Microscopy, Boron Nitride

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Brian LeRoy
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Report Title

Final Report: Understanding and controlling the electronic properties of graphene using scanning probe microscopy

ABSTRACT

This project has been focused on understanding and controlling the electronic properties of graphene using scanning tunneling spectroscopy and optical spectroscopy. By using boron nitride as a substrate underneath graphene we have significantly improved the device quality. We have found that the periodic potential from the boron nitride can modify the band structure of the graphene. The boron nitride also changes the Raman spectrum of the graphene. We have also explored the role of adding additional layers to graphene and different stacking configurations. A third aspect of the project has studied modification
of the graphene band structure through femtosecond laser pulses.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
05/01/2012	11.00	W. Bao, Z. Zhao, C. N. Lau, B. J. LeRoy, A. Deshpande. Mapping the Dirac point in gated bilayer graphene, Applied Physics Letters, (12 2009): 243502. doi: 10.1063/1.3275755
07/17/2014	19.00	Brian J. LeRoy, Adam T. Roberts, Rolf Binder, Nai H. Kwong, Dheeraj Golla, Daniel Cormode, Henry O. Everitt, Arvinder Sandhu. Optical Characterization of Electron-Phonon Interactions at the Saddle Point in Graphene, Physical Review Letters, (05 2014): 187401. doi: 10.1103/PhysRevLett.112.187401
07/17/2014	20.00	Matthew Yankowitz, Joel I-Jan Wang, A. Glen Birdwell, Yu-An Chen, K. Watanabe, T. Taniguchi, Philippe Jacquod, Pablo San-Jose, Pablo Jarillo-Herrero, Brian J. LeRoy. Electric field control of soliton motion and stacking in trilayer graphene, Nature Materials, (04 2014): 0. doi: 10.1038/nmat3965
07/21/2014	21.00	Matthew Yankowitz, Joel I-Jan Wang, Suchun Li, A. Glen Birdwell, Yu-An Chen, Kenji Watanabe, Takashi Taniguchi, Su Ying Quek, Pablo Jarillo-Herrero, Brian J. LeRoy. Band structure mapping of bilayer graphene via quasiparticle scattering, APL Materials, (09 2014): 92503. doi:
08/26/2013	14.00	Matthew Yankowitz, Fenglin Wang, Chun Ning Lau, Brian J. LeRoy. Local spectroscopy of the electrically tunable band gap in trilayer graphene, Physical Review B, (04 2013): 165102. doi: 10.1103/PhysRevB.87.165102
08/26/2013	15.00	Dheeraj Golla, Kanokporn Chattrakun, Kenji Watanabe, Takashi Taniguchi, Brian J. LeRoy, Arvinder Sandhu. Optical thickness determination of hexagonal boron nitride flakes, Applied Physics Letters, (04 2013): 161906. doi: 10.1063/1.4803041
08/29/2012	13.00	Matthew Yankowitz, Jiamin Xue, Daniel Cormode, Javier D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, Pablo Jarillo-Herrero, Philippe Jacquod, Brian J. LeRoy. Emergence of superlattice Dirac points in graphene on hexagonal boron nitride, Nature Physics, (03 2012): 382. doi: 10.1038/nphys2272
08/30/2011	6.00	Aparna Deshpande, Wenzhong Bao, Zeng Zhao, Chun Ning Lau, Brian LeRoy. Spatial Mapping of the Dirac Point in Monolayer and Bilayer Graphene, IEEE Transactions on Nanotechnology, (01 2011): 88. doi: 10.1109/TNANO.2010.2057256
08/30/2011	10.00	Wenzhong Bao, Gang Liu, Zeng Zhao, Hang Zhang, Dong Yan, Aparna Deshpande, Brian LeRoy, Chun Ning Lau. Lithography-free fabrication of high quality substrate-supported and freestanding graphene devices, Nano Research, (03 2010): 98. doi: 10.1007/s12274-010-1013-5
08/30/2011	9.00	A. Deshpande, W. Bao, Z. Zhao, C. Lau, B. LeRoy. Imaging charge density fluctuations in graphene using Coulomb blockade spectroscopy, Physical Review B, (04 2011): 155409. doi: 10.1103/PhysRevB.83.155409
08/30/2011	8.00	Adam Roberts, Daniel Cormode, Collin Reynolds, Ty Newhouse-Illige, Brian J. LeRoy, Arvinder S. Sandhu. Response of graphene to femtosecond high-intensity laser irradiation, Applied Physics Letters, (08 2011): 51912. doi: 10.1063/1.3623760

08/30/2011	7.00	Jiamin Xue, Javier Sanchez-Yamagishi, Danny Bulmash, Philippe Jacquod, Aparna Deshpande, K. Watanabe, T. Taniguchi, Pablo Jarillo-Herrero, Brian J. LeRoy. Scanning tunnelling microscopy and spectroscopy of ultra-flat graphene on hexagonal boron nitride, Nature Materials, (02 2011): 282. doi: 10.1038/nmat2968
11/26/2013	17.00	Kanokporn Chattrakun, Shengqiang Huang, Kenji Watanabe, Takashi Taniguchi, Arvinder Sandhu, Brian LeRoy. Gate dependent Raman spectroscopy of graphene on hexagonal boron nitride, Journal of Physics: Condensed Matter, (11 2013): 505304. doi:

TOTAL: **13**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

“Electronic properties of graphene on boron nitride.” DyProSo XXXIV Conference, Vienna Austria, September 2013 (Talk given by PI).
“Local electronic properties of graphene.” AVS Symposium, Long Beach CA, October 2013 (Talk given by PI).
“Imaging and spectroscopy of graphene heterostructures,” March Meeting of the American Physical Society, Denver CO, March 2014 (Talk given by PI).
“Electronic field control of stacking-order solitons in trilayer graphene,” March Meeting of the American Physical Society, Denver CO, March 2014 (Talk given by Matthew Yankowitz, graduate student).
“Gated Raman spectroscopy of twisted bilayer graphene,” March Meeting of the American Physical Society, Denver CO, March 2014 (Talk given by Shengqiang Huang, graduate student).

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
01/21/2011	5.00	Jiamin Xue, Javier Sanchez-Yamagishi, Danny Bulmash, Philippe Jacquod, Aparna Deshpande, K. Watanabe, T. Taniguchi, Pablo Jarillo-Herrero, Brian J. LeRoy. STM spectroscopy of ultra-flat graphene on hexagonal boron nitride, Nature Materials (01 2011)
02/13/2012	12.00	Matthew Yankowitz, Jiamin Xue, Daniel Cormode, Javier D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, Pablo Jarillo-Herrero, Philippe Jacquod, Brian J. LeRoy. Emergence of Superlattice Dirac Points in Graphene on Hexagonal Boron Nitride, Nature Physics (11 2011)
08/26/2013	16.00	Kanokporn Chattrakun, Shengqiang Huang, Kenji Watanabe, Takashi Taniguchi, Arvinder Sandhu, Brian J. LeRoy. Gate dependent Raman spectroscopy of grapheneon hexagonal boron nitride, Journal of Physics: Condensed Matter (08 2013)
09/23/2010	4.00	A. Deshpande, W. Bao, H. Zhang, Z. Zhao, C.N. Lau, B.J. LeRoy. Spatial mapping of charge fluctuations in graphene using Coulomb blockade spectroscopy, (09 2010)
11/02/2009	1.00	B. LeRoy, A. Deshpande, W. Bao, Z. Zhao, C. Lau. Mapping the Dirac point in gated bilayer graphene, (10 2009)
11/26/2013	18.00	Adam Roberts, Rolf Binder, Nai Kwong, Dheeraj Golla, Daniel Cormode, Brian LeRoy, Henry Everitt, Arvinder Sandhu. Optical characterization of electron-phonon interactions at the saddle point in graphene, ArXiv: 1310.2683 (10 2013)
12/03/2009	2.00	A. Deshpande, W. Bao, Z. Zhao, C. Lau, B. LeRoy. Spatial mapping of the Dirac point in monolayer and bilayer graphene, (12 2009)
12/15/2009	3.00	W. Bao, G. Liu, Z. Zhao, H. Zhang, D. Yan, A. Deshpande, B. LeRoy, C. Lau. Lithography-free Fabrication of High Quality Substrate-supported and Freestanding Graphene devices, (12 2009)

TOTAL: **8**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

METHODS FOR MODIFYING CRYSTAL STRUCTURE AND DEVICES COMPRISING THE SAME

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Matthew Yankowitz	1.00	
Shengqiang Huang	1.00	
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Brian LeRoy	0.04	No
FTE Equivalent:	**0.04**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

5 Methods for modifying crystal structure and devices

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) Y

Foreign Countries of application (5g-2):

5a: Matthew Yankowitz

5f-1a: University of Arizona

5f-c: 1118 E. 4th St.

Tucson AZ 85721

5a: Brian LeRoy

5f-1a: University of Arizona

5f-c: 1118 E. 4th St.

Tucson AZ 85721

Scientific Progress

See Attachment

Technology Transfer

Understanding and controlling the electronic properties of graphene using scanning probe microscopy

As discussed below, this project was focused on understanding and controlling the electronic properties of graphene using microscopy techniques. The main project used scanning probe microscopy and optical spectroscopy in the PI's (Brian LeRoy) group to study the fundamental electronic properties of graphene devices at the atomic scale. There was also a subcontract in the first year of the project with Leonard Franklin Register for the simulation of transport through monolayer and bilayer graphene devices.

The experimental aspects of this project have focused on using scanning tunneling spectroscopy to map the local density of states in monolayer, bilayer and trilayer graphene devices. In these devices, we have found the existence of electron and hole doped regions. By comparing atomically resolved topographic images with local density of states maps we were able to show that the doped regions were due to charged impurities in the substrate. The presence of these impurities limits the mobility of graphene devices and ultimately the speed that can be achieved. In bilayer devices, we showed that the electric field from the STM tip is able to controllably open a band gap. We were also able to determine the band structure of the graphene as a function of the electric field. A similar effect occurs in trilayer devices but it depends on the stacking arrangement of the three layers. This allows an electric field to control the stacking arrangement of trilayer graphene and thus change it from a semi-metal to a semiconductor. Expanding on our work characterizing graphene devices, we have also looked at the effect of changing the graphene substrate. We have found that using boron nitride for a substrate significantly improves device performance. Furthermore, the boron nitride is also able to modify the band structure of the graphene opening the way to controlling the electrons in graphene devices by tailoring the substrate. Our latest work has examined other ways to control the band structure of graphene either through the creation of layered heterostructures or pulses of light.

The theoretical aspects of the project focused on modeling dynamic evolution of electron wavefunctions through time-dependent simulation in graphene layers, and on the formation of many-body condensates in two graphene layers separated by a dielectric, and calculation of the corresponding critical currents between the layers—the maximum currents the condensate can support before collapsing. Ultimately the process of collapse, itself, involves a time-dependent instability, so that modeling it requires the merging of these two components of the research.

The work on this project resulted in 13 ARO supported papers from the PI's group during the funding period:

"Mapping the Dirac point in gated bilayer graphene," A. Deshpande, W. Bao, Z. Zhao, C.N. Lau, and B.J. LeRoy, *Applied Physics Letters* **95**, 243502 (2009).

"Lithography-free fabrication of high quality substrate-supported and suspended graphene devices," W. Bao, G. Liu, Z. Zhao, D. Yan, A. Deshpande, B.J. LeRoy, and C.N. Lau, *Nano Research* **3**, 98 (2010).

“Spatial mapping of the Dirac point in monolayer and bilayer graphene,” A. Deshpande, W. Bao, Z. Zhao, C.N. Lau, and B.J. LeRoy, *IEEE Transactions on Nanotechnology* **10**, 88 (2011).

“Imaging charge density fluctuations in graphene using Coulomb blockade spectroscopy,” A. Deshpande, W. Bao, Z. Zhao, C.N. Lau and B.J. LeRoy, *Physical Review B* **83**, 155409 (2011).

“Scanning tunnelling microscopy and spectroscopy of ultra-flat graphene on hexagonal boron nitride,” J. Xue, J. Sanchez-Yamagishi, D. Bulmash, P. Jacquod, A. Deshpande, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, and B.J. LeRoy, *Nature Materials* **10**, 282 (2011).

“Response of graphene to femtosecond high-intensity laser irradiation,” A. Roberts, D. Cormode, C. Reynolds, T. Newhouse-Illige, B.J. LeRoy, and A. Sandhu, *Applied Physics Letters* **99**, 051912 (2011).

“Emergence of superlattice Dirac point in graphene on hexagonal boron nitride,” M. Yankowitz, J. Xue, D. Cormode, J. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, P. Jarillo-Herrero, P. Jacquod, and B.J. LeRoy, *Nature Physics* **8**, 382 (2012).

“Local spectroscopy of the electrically tunable band gap in trilayer graphene,” M. Yankowitz, F. Wang, C.N. Lau, B.J. LeRoy, *Physical Review B* **87**, 165102 (2013).

“Optical thickness determination of hexagonal boron nitride flakes,” D. Golla, K. Chattrakun, K. Watanabe, T. Taniguchi, B.J. LeRoy, and A. Sandhu, *Applied Physics Letters* **102**, 161906 (2013).

“Gate dependent Raman spectroscopy of graphene on hexagonal boron nitride,” K. Chattrakun, S. Huang, K. Watanabe, T. Taniguchi, A. Sandhu, and B.J. LeRoy, *Journal of Physics: Condensed Matter* **25**, 505304 (2013).

“Electric field control of soliton motion and stacking in trilayer graphene,” M. Yankowitz, J. I.-J. Wang, A.G. Birdwell, Y.-A. Chen, K. Watanabe, T. Taniguchi, P. Jacquod, P. San-Jose, P. Jarillo-Herrero, and B.J. LeRoy, *Nature Materials* advance online publication 28 April 2014 (DOI: 10.1038/nmat3965)**.**

“Optical characterization of electron-phonon interactions at the saddle point in graphene,” A.T. Roberts, R. Binder, N.H. Kwong, D. Golla, D. Cormode, B.J. LeRoy, H.O. Everitt, and A. Sandhu, *Physical Review Letters* **112**, 187401 (2014).

“Band structure mapping of bilayer graphene via quasiparticles scattering,” M. Yankowitz, J. I.-J. Wang, S. Li, A.G. Birdwell, Y.-A. Chen, K. Watanabe, T. Taniguchi, S.Y. Quek, P. Jarillo-Herrero, and B.J. LeRoy, *APL Materials* **2**, 092503 (2014).

This project helped to support five Ph.D. students, Dipanjan Basu (UT-Austin), who successfully defended his Ph.D. thesis (8/27/2010), Dharmendar Reddy (UT-Austin), Daniel Cormode (Arizona), Shengqiang Huang (Arizona) and Matthew Yankowitz (Arizona). Dharmendar Reddy was recruited for an internship at IBM (could not refuse in this economy). Daniel Cormode took at job at Solon Corporation due to family reasons. He received an M.S. for his work at Arizona. The other 2 students are continuing to work in the PI’s group. The work has also

provided support for the PI of the main project, Brian LeRoy and of the subcontract, Leonard Franklin Register. A subaward of the project, through the High School Apprenticeship Program (HSAP) provided stipends to two high school students during the summer of 2010, Braden Smith and Reilly Bello. Also, Aparna Deshpande was a post-doctoral researcher working in Prof. LeRoy's group. She performed much of the early experimental work on this project and the project supported all of the costs associated with her work. However, her salary was paid through startup funds provided by the University of Arizona. Her contract ended on 08/01/2010 and she is now an assistant professor at the Indian Institute of Science Education and Research in Pune.

Our work since the last report has had two main focuses, (1) looking at ways to measure and modify the electronic properties of graphene with additional layers. (2) Optical characterization of graphene at high energies near the saddle point. In the following sections, we will discuss in detail the experimental progress that was made on the project since the last report.

Control of stacking in trilayer graphene

The crystal structure of a material determines its electrical properties. Trilayer graphene comes in two inequivalent stacking configurations, ABA (Bernal) or ABC (Rhombohedral). These configurations are nearly degenerate in energy and both are found in naturally occurring graphite. The ABA structure is symmetric and therefore a vertical electric field is unable to open a band gap in the graphene. This is similar to monolayer graphene which remains conductive in the presence of an electric field. ABC stacked graphene on the other hand is not symmetric and a perpendicular electric field is able to open a band gap. Furthermore, the dispersion relations of the two different stacking orders are different. ABA trilayer graphene resembles a combination of monolayer and bilayer dispersion relations. ABC trilayer graphene has a single cubic dispersion at low energy. Using scanning tunneling spectroscopy measurements we have measured the local density of states in the two different stacking configurations.

Figure 1 shows representative spectroscopy measurements on the two different stacking arrangements of trilayer graphene. Figure 1(a) shows ABA stacked graphene which remains metallic as the electric field is increased. On the other hand, figure 1(b) shows the results for ABC stacked trilayer graphene. At the largest electric fields (near the top of the figure), a large band gap is opened. The band edges are marked by the vertical lines whose separation increases as a function of electric field.

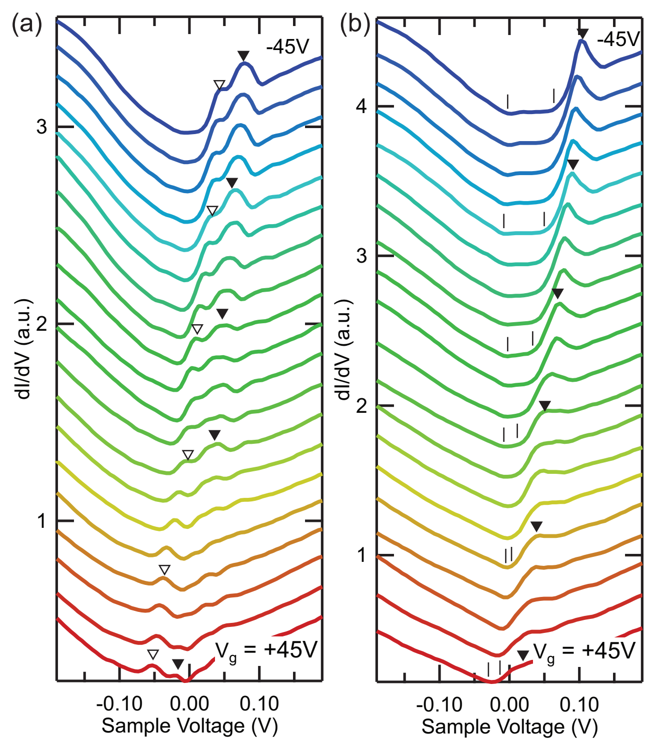

Figure 1 (a) Spectroscopy on ABA stacked trilayer graphene as a function of electric field showing that it remains metallic. (b) Spectroscopy on ABC stacked trilayer graphene as a function of electric field showing the opening of a band gap. The band edges are indicated by the vertical lines.

In graphene flakes with both stacking arrangements, there is a region of strain (domain wall) separating the two different stacking configurations. We have shown that when an electric field is applied to trilayer graphene, the rhombohedral (ABC) stacking is preferred and therefore the domain wall moves (Figure 2) so that the rhombohedral-stacked area is maximized. This occurs because opening a band gap in the material lowers its energy, which favors the rhombohedral stacking. As the graphene transitions to ABC stacking it becomes a semiconductor with a tunable band gap. The ability to control the crystal structure of a material with an external electric field opens the way to several different device possibilities. This behavior is also critical to other van der Waals heterostructures where the relative orientation between layers determines their electronic properties.

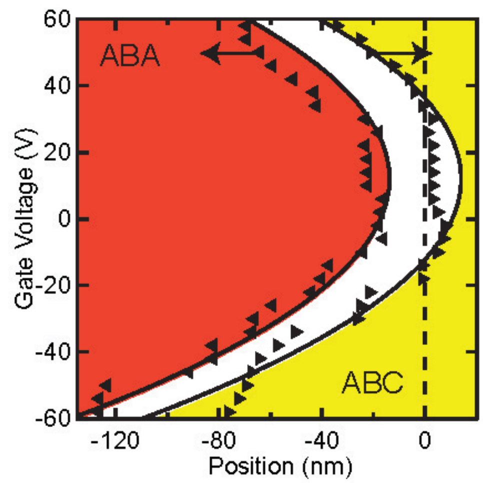

Figure 2. The boundary between ABA and ABC stacked graphene moves with electric field. The sample becomes ABC stacked as the electric field increases.

This work resulted in an ARO supported publication that was published in *Nature Materials* in 2014, "Electric field control of soliton motion and stacking in trilayer graphene," M. Yankowitz, J. I.-J. Wang, A.G. Birdwell, Y.-A. Chen, K. Watanabe, T. Taniguchi, P. Jacquod, P. San-Jose, P. Jarillo-Herrero, and B.J. LeRoy.

Band structure mapping in bilayer graphene

One drawback for using monolayer graphene in digital electronics applications is the lack of a band gap. However, in Bernal stacked bilayer graphene a band gap can be opened with the application of an electric field. Without an electric field, the band structure of bilayer graphene is such that the conduction and valence bands are hyperbolic and touch at only the K and K' point in the Brillouin zone. The bands can be described using a tight binding model with only a few parameters such as the in-plane hopping and the coupling to the nearest neighbors out of the plane. As the electric field is increased, the bands move and a band gap is opened. This causes the effective masses of the electrons and holes to increase.

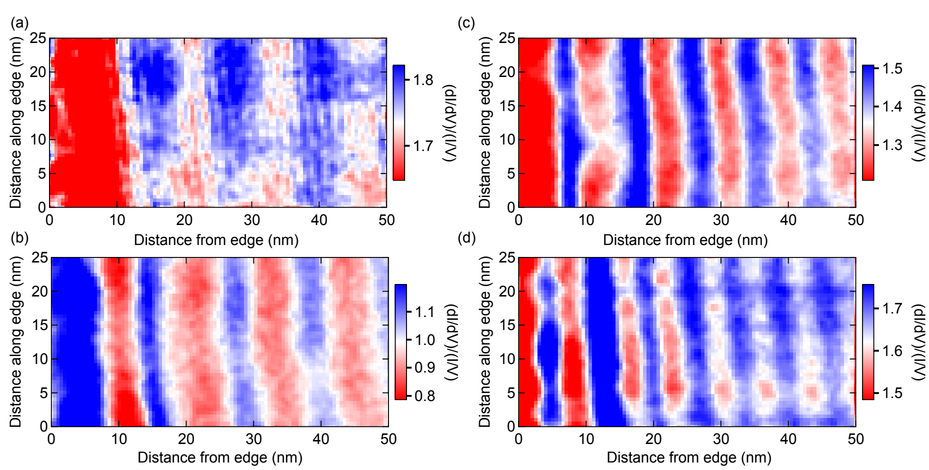

Figure 3. Standing waves in bilayer graphene at different energies. The wavelength changes giving a direct measurement of the dispersion relation of the graphene.

Using scanning tunneling spectroscopy, we have mapped the

band structure of bilayer graphene as a function of electric field. This was done by measuring the wavelength of standing waves in graphene caused by electrons that have undergone scattering events. In this particular case, we have studied scattering from a bilayer/trilayer interface. Figure 3 shows the results for four different energies in both the conduction and valence bands. The wavelength of the standing waves as a function of energy gives the dispersion relation of the bilayer graphene.

Figure 4 shows the measured dispersion relation as a function of electric field. We find that there is an asymmetry between the conduction and valence bands. The effective mass of the electrons is smaller than for holes. We also find, in agreement with our previous measurements, the opening of a band gap as the electric field increases. These results can be captured with a simple tight binding model which explains not only the asymmetry between the bands but also their evolution with electric field.

This work has resulted in an ARO supported publication that was published in *APL Materials* in 2014, "Band structure mapping of bilayer graphene using quasiparticle scattering," M. Yankowitz, J. I.-J. Wang, S. Li, A.G. Birdwell, Y.-A. Chen, K. Watanabe, T. Taniguchi, S.Y. Quek, P. Jarillo-Herrero, and B.J. LeRoy.

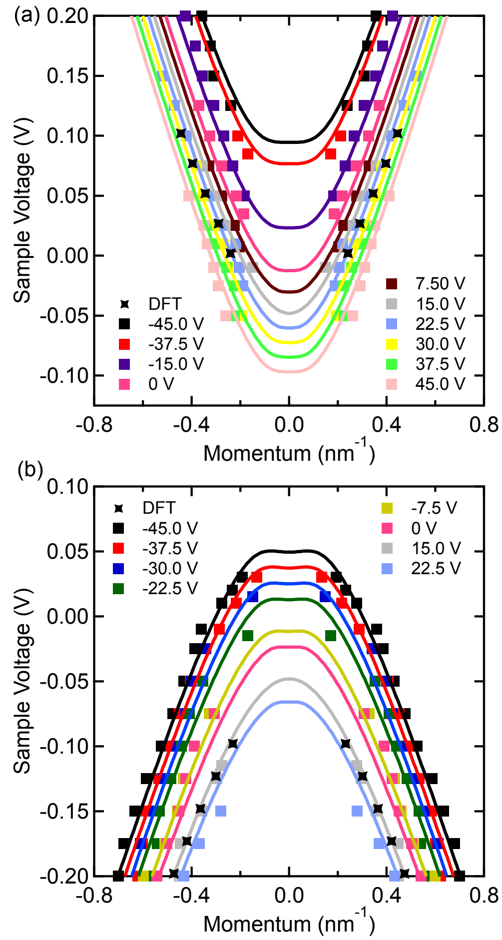

Figure 4. Dispersion relation for (a) conduction and (b) valence band of bilayer graphene as a function of electric field. The points are measured data from the scattering experiment and the solid lines are the band structure from the tight binding model.

Optical modification of the graphene band structure

We have also continued our work to understand the optical response of graphene under femtosecond laser irradiation. This work is an experimental collaboration with Prof. Arvinder Sandhu also in the physics department at the University of Arizona, Henry Everitt at the Army AMRDEC in Huntsville, AL and theoretical calculations from Prof. Rolf Binder in the College of Optical Sciences at the University of Arizona. The PI's group has provided graphene samples and the optical spectroscopy measurements have been carried out in the Sandhu and Everitt labs.

Many-body interactions between quasi-particles play an important role in determining the band structure and opto-electronic applications of materials. For example, the rise of semiconductors was followed by efforts to understand how their band structure is modified by carrier-carrier and carrier-phonons interactions and mechanisms such as doping, quantum confinement, carrier injection, and temperature control were extensively employed to control their properties. Many-body interactions play an even more important role in graphene, due to the

reduced Coulomb screening in two-dimensional systems compared to bulk materials. Understanding these interactions is important due to the immense application potentials offered by graphene.

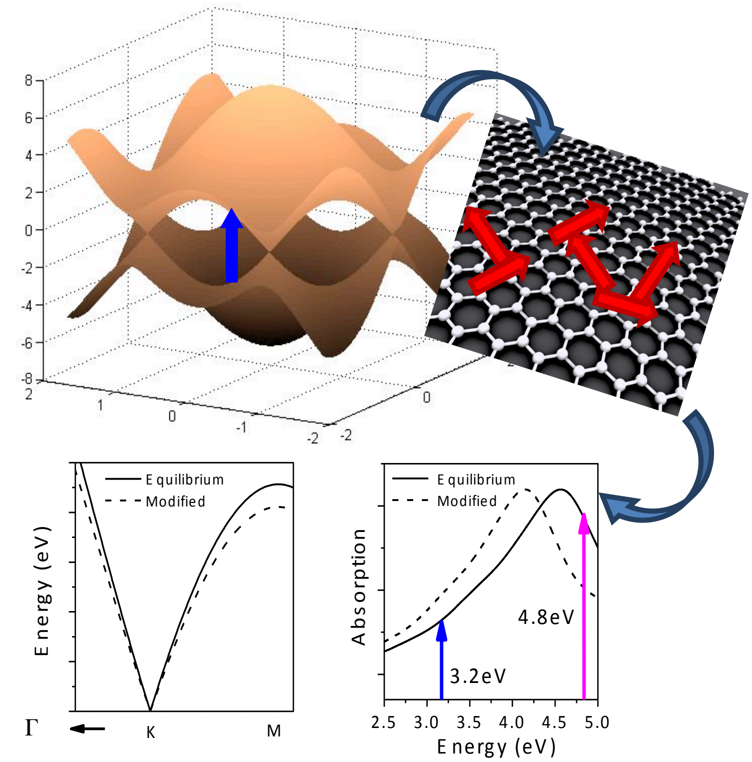

Figure 5. Pump-probe studies of graphene have observed a dynamic modification of the band-structure caused by photo excited carriers and the subsequent creation of phonons.

We have subjected graphene to an ultrashort pump laser pulse at 4.77 eV, then observed its response over a wide range of energies and timescales using a delayed probe pulse. Through a differential measurement of the transmission of the probe, we have observed a dynamic band structure modification caused by the photo-excited carriers and the subsequently generated phonons. These measurements allow us to quantify the many-body effects such as electron-phonon coupling in non-equilibrium graphene. The ability to perform femtosecond spectroscopy measurements along with in-situ Raman measurements on graphene, opens an entire new set of measurements on the time-resolved properties of graphene devices. These measurements complement our electronic spectroscopy measurements in the scanning tunneling microscope.

This work has resulted in an ARO supported publication that was published in *Physical Review Letters* in 2014, "Optical characterization of electron-phonon interactions at the saddle point in graphene," A. Roberts, R. Binder, N.-H. Kwang, D. Golla, D. Cormode, B.J. LeRoy, H. Everitt, and A. Sandhu.